3. Methods of Preparation

2-Bromopyridine has been made by direct bromination of pyridine;[2] from N-methyl-2-pyridone with phosphorus pentabromide and phosphorus oxybromide;[3] from 2-aminopyridine by diazotization with amyl nitrite in 20% hydrobromic acid;[4] from sodium 2-pyridinediazotate by solution in concentrated hydrobromic acid;[5] and from 2-aminopyridine by diazotization in the presence of bromine and concentrated hydrobromic acid.[6] The method described here is essentially that of Craig.

References

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[5] Tschitschibabin and Tjashelowa, *J. Russ. Phys. Chem. Soc.*, **50**, 495 (1918) [*Chem. Zentr.*, **1923** III, 1021].

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n-BUTYL ACRYLATE

(Acrylic acid, *n*-butyl ester)

$$CH_2{=}CHCOOCH_3 + C_4H_9OH \rightarrow CH_2{=}CHCOOC_4H_9 + CH_3OH$$

Submitted by CHESSIE E. REHBERG.
Checked by H. R. SNYDER and FRED E. BOETTNER.

1. Procedure

In a 2-l. two-necked round-bottomed flask having a capillary ebullator tube in one neck (Note 1) are placed 371 g. (5 moles)

butyl alcohol, 861 g. (10 moles) of methyl acrylate, 20 g. of hydroquinone, and 10 g. of *p*-toluenesulfonic acid (Note 2). The flask is attached to an all-glass fractionating column, preferably one without packing such as the Vigreux type (Note 3), and the solution is heated to boiling in an oil bath. The column is operated under total reflux until the temperature of the vapors at the still head falls to 62–63°, which is the boiling point of the methanol-methyl acrylate azeotrope (Note 4). This azeotrope is then distilled as rapidly as it is formed, the temperature at the still head not being allowed to exceed 65°. When the production of methanol has become very slow (6–10 hours), the excess methyl acrylate is distilled, and the butyl acrylate is then distilled, preferably at 10–20 mm. It boils at 39°/10 mm., 84–86°/101–102 mm., and at about 145° at atmospheric pressure. The yield is 500 to 600 g. (78–94%) (Note 5).

2. Notes

1. The capillary is used to introduce a gas to prevent bumping and superheating during the vacuum distillation of the product. As air has some tendency to catalyze polymerization of the acrylic ester, if it is introduced through the capillary the amount must be as small as possible. The gas introduced should be an inert one, such as carbon dioxide or nitrogen. If polymerization is troublesome, it may be advantageous to pass in a slow stream of carbon dioxide through the capillary during the entire reaction period.

2. Sulfuric acid is also a very satisfactory catalyst; aluminum alkoxides also are useful, especially when the alcohols would be adversely affected by strong acids. Sodium alkoxides produce undesirable side reactions and give lower yields. When alkaline catalysts are employed, an alkaline polymerization inhibitor, such as *p*-phenylenediamine or phenyl-β-naphthylamine, should be used instead of hydroquinone.

3. The fractionating column should be one which can be cleaned readily if a polymer is formed in it. A large number of plates is not required, though the column should be capable of separating the methanol-methyl acrylate azeotrope (b.p. 62–63°) from methyl acrylate (b.p. 80°) and butanol (b.p. 117°) from butyl acrylate (b.p. 145°). The necessity of effecting the latter separation can be practically eliminated by allowing the reaction to go virtually to completion, all the butanol thus being consumed. This can be done by extending the reaction period as long as reaction occurs and by adding a considerable excess of methyl acrylate. Instead of the twofold excess specified, three or four times the theoretical amount may be used with benefit. The larger amount is especially desirable when the acrylate of a relatively unreactive alcohol is being prepared.

4. The methanol-methyl acrylate azeotrope contains about 45% methyl acrylate, which can be recovered by washing out the methanol with a large volume of water or brine; the acrylate is purified by drying and distilling. An inhibitor, such as hydroquinone, should always be added to any acrylic ester before attempting to distil it, and, unless it is stored in a refrigerator, the distilled ester should not be kept more than a few hours without the addition of a small amount (0.1–1.0%) of an inhibitor.

5. Yields of the primary alkyl acrylates vary somewhat, owing to occasional losses through formation of polymer, but are usually in the range of 85–99%. Some secondary alcohols react very slowly, others readily. The method has been applied to more than fifty alcohols, some of which (with percentage yields) are listed below: ethyl, 99%; isopropyl, 37%; *n*-amyl, 87%; isoamyl, 95%; *n*-hexyl, 99%; 4-methyl-2-pentyl, 95%; 2-ethylhexyl, 95%; capryl, 80%; lauryl, 92%; myristyl, 90%; allyl, 70%; furfuryl, 86%; citronellyl, 91%; cyclohexyl, 93%; benzyl, 81%; β-ethoxyethyl, 99%; β-(β-phenoxyethoxy)ethyl (from diethylene glycol monophenyl ether), 88%.

3. Methods of Preparation

n-Butyl acrylate has been prepared by direct esterification,[1] by debromination of *n*-butyl α,β-dibromopropionate with zinc,[2] by treatment of either butyl β-chloropropionate [1] or butyl β-bromopropionate [1] with diethylaniline, and by the pyrolysis of butyl β-acetoxypropionate.[3] Direct esterification and alcoholysis of methyl or ethyl acrylate have been recommended for the preparation of the higher alkyl acrylates.[4]

References

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DI-(*p*-CHLOROPHENYL)-ACETIC ACID

(Acetic acid, di-(*p*-chlorophenyl))

$$(p\text{-}ClC_6H_4)_2CHCCl_3 + KOH \rightarrow (p\text{-}ClC_6H_4)_2C{=}CCl_2 + KCl + H_2O$$

$$(p\text{-}ClC_6H_4)_2C{=}CCl_2 + 3KOH \rightarrow (p\text{-}ClC_6H_4)_2CHCOOK + 2KCl + H_2O$$

$$(p\text{-}ClC_6H_4)_2CHCOOK + H_2SO_4 \rightarrow (p\text{-}ClC_6H_4)_2CHCOOH + KHSO_4$$

Submitted by Oliver Grummitt, Allen Buck, and Richard Egan.
Checked by Lee Irvin Smith, R. T. Arnold, and Paul N. Craig.

1. Procedure

A mixture of 400 ml. of diethylene glycol (Note 1) and 49.5 g. (0.14 mole) of 1,1-di-(*p*-chlorophenyl)-2,2,2-trichloroethane